

## REVISION OF THE CRYSTALLOGRAPHIC DATA OF POLYMORPHIC $\text{Y}_2\text{Si}_2\text{O}_7$ AND $\text{Y}_2\text{SiO}_5$ COMPOUNDS

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This article revises, analyses, completes and summarizes the crystalline structure of all the  $\text{Y}_2\text{Si}_2\text{O}_7$  and  $\text{Y}_2\text{SiO}_5$  polymorphs by combination of diffraction and crystallographic data with spectroscopic MAS-NMR data published up to now.

**Keywords:** Crystal structure; Polymorphism; Silicates; Yttrium; MAS-NMR spectroscopy

### INTRODUCTION

Phase relationships in rare earth (RE) and yttrium silicates have been extensively studied for both, applied and academic interests. They were originally studied because of an interest in laser materials and in high-energy phosphors based on RE doped yttrium silicate (Bondar *et al.*, 1969). Recently, interest in these systems has been renewed because of the improved mechanical properties of  $\text{Si}_3\text{N}_4$  and SiC when yttrium and other RE oxides are used as sintering additives (Kim *et al.*, 2001, 2002; Hong *et al.*, 2002; Meléndez Martínez and Domínguez-Rodríguez, 2004). Yttrium silicate compounds show an extensive polymorphism and they constitute clear examples of reconstructive phase transitions. Yttrium orthosilicate ( $\text{Y}_2\text{SiO}_5$ ) exhibits two different polymorphs with temperature (namely, X1 and X2), while yttrium disilicate ( $\text{Y}_2\text{Si}_2\text{O}_7$ ) shows up to six polymorphs ( $\gamma$ ,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ , and, possibly,  $z$ ) (Felsche, 1973).

The need for reliable crystallographic information on the different polymorphs led Liddell and Thompson (1986) to summarize X-ray diffraction data for all these phases and to identify and correct errors which appeared in the literature. Since then, new diffraction data, from both X-ray and neutron sources, have been compiled

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for both compounds  $\text{Y}_2\text{SiO}_5$  and  $\text{Y}_2\text{Si}_2\text{O}_7$ , and an elevated number of JCPDS (Joint Committee for Powder Diffraction Data) charts and entries in the Inorganic Crystal Structure Database (ICSD) exist at present. Many of them do not make any reference to the type of polymorph described and there are several different charts referred to the same polymorph, with different information. In addition, there seems to be some controversy about the space groups assigned to some of the  $\text{Y}_2\text{Si}_2\text{O}_7$  polymorphs and the number of crystallographic sites of Y atoms varies from one description to the other. All this makes it difficult to do a comprehensive analysis of the existing data. Spectroscopic techniques, such as Nuclear Magnetic Resonance (NMR), have proved to be extremely useful for structure elucidation in solid materials. In fact, well resolved  $^{89}\text{Y}$  MAS-NMR spectra have been published for all the  $\text{Y}_2\text{Si}_2\text{O}_7$  and  $\text{Y}_2\text{SiO}_5$  polymorphs (Dupree and Smith, 1988; Becerro *et al.*, 2004) and  $^{29}\text{Si}$  MAS NMR data exist for five  $\text{Y}_2\text{Si}_2\text{O}_7$  polymorphs (Parmentier *et al.*, 2000; Becerro *et al.*, 2003) and for  $\text{X}_2\text{-Y}_2\text{SiO}_5$  (Dupree *et al.*, 1988).

The aim of the present study is to revise, analyse, clarify and summarize the structure of all the  $\text{Y}_2\text{Si}_2\text{O}_7$  and  $\text{Y}_2\text{SiO}_5$  polymorphs by combination of the diffraction and crystallographic data described in the JCPDS and ICSD charts, respectively, and the spectroscopic NMR data. In addition, the  $^{29}\text{Si}$  MAS-NMR spectrum of  $\text{X1-Y}_2\text{SiO}_5$  is published here.

## RESULTS AND DISCUSSION

### $\text{Y}_2\text{Si}_2\text{O}_7$ Polymorphs

Structurally, rare-earth binary disilicates are well known for their polymorphism (Feslche, 1973). Ito and Johnson (1968) demonstrated that yttrium disilicate shows the same four polymorphs as those described for its homolog  $\text{Ho}_2\text{Si}_2\text{O}_7$  (i.e.,  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$  or  $B$ ,  $C$ ,  $D$  and  $E$ , respectively, in order of stability with increasing temperature), plus an additional low-temperature phase, the yttrialite low form, also called  $y\text{-Y}_2\text{Si}_2\text{O}_7$ . In addition, they submitted unindexed powder data for a phase called  $z$ -phase to the JCPDS index (card 21-1459) defining it as a low temperature modification of  $\text{Y}_2\text{Si}_2\text{O}_7$  stable below  $1030^\circ\text{C}$ . Liddell and Thompson (1986) find it reasonable that this should be a hydrate of  $\text{Y}_2\text{Si}_2\text{O}_7$ . To our knowledge, no new data or further specimens of this phase have been obtained and, for that reason, it has not been taken into account for the present work. All the yttrium disilicate polymorphs, except the  $\alpha$  one, which will be described below, consist of Si tetrahedra pairwise joined to form diortho groups ( $\text{Si}_2\text{O}_7$ ) with a Si–O–Si bond angle which varies from one polymorph to the other.

### $y\text{-Y}_2\text{Si}_2\text{O}_7$ Polymorph

The crystalline structure of  $y\text{-Y}_2\text{Si}_2\text{O}_7$  has only been described by Batalieva and Pyatenko (1972) in the monoclinic space group  $P2_1/m$  with cell dimensions:  $a = 7.50(3) \text{ \AA}$ ,  $b = 8.06(3) \text{ \AA}$ ,  $c = 5.02(2) \text{ \AA}$  and  $\beta = 112.0(5)^\circ$ . Diortho groups ( $\text{Si}_2\text{O}_7$ ) show a Si–O–Si bond angle of  $134^\circ$  and share all the oxygens with the yttrium octahedra, except the bridging one (Fig. 1a). The unit cell contains two equally populated Y sites, both octahedrally coordinated (Fig. 1b) and two Si sites, with tetrahedral

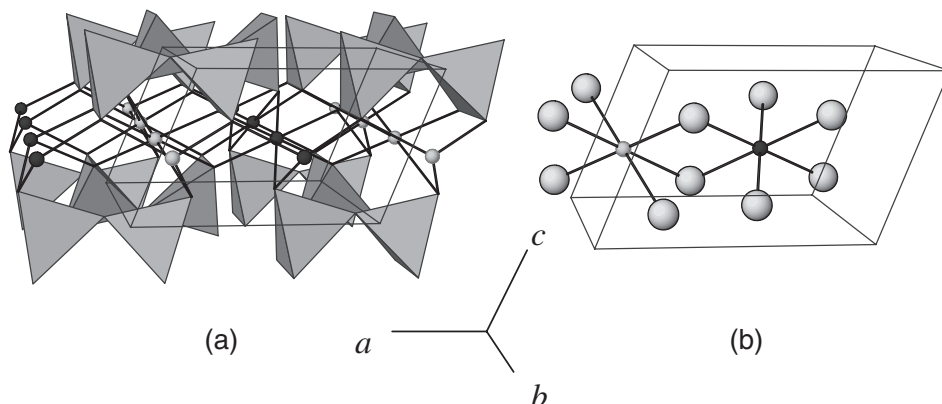


FIGURE 1 (a) The crystal structure of  $\gamma$ - $\text{Y}_2\text{Si}_2\text{O}_7$  based on the data of Batalieva *et al.* (1972). Polyhedra represent diortho groups  $(\text{Si}_2\text{O}_7)^{6-}$  and the dark and light grey spheres represent the two crystallographically different Y sites. (b) Detail of the coordination of Y to O.

coordination to oxygen. These data are described in the ICSD chart 28004 (although it is called “yttrialite gamma”) and the calculated diffraction pattern is included, as “Yttrialite-Y”, in JCPDS chart 74-1994. On the other hand, JCPDS chart 32-1448 gives position and intensity of unindexed reflections for “gamma- $\text{Y}_2\text{Si}_2\text{O}_7$ ” but they are the same as in JCPDS chart 74-1994, except that JCPDS 32-1448 shows three extra reflections located at 2.98, 2.90 and 2.79 Å. Finally, JCPDS chart 45-42 is to replace JCPDS 32-1448; however it describes the phase in the orthorhombic space group  $\text{Aba2}$ , and, in fact, the number of reflections is lower than in JCPDS 32-1448. The  $^{29}\text{Si}$  MAS-NMR spectrum of  $\gamma$ - $\text{Y}_2\text{Si}_2\text{O}_7$  (Becerro *et al.*, 2003) consists of two peaks at  $-83.2$  ppm and  $-85.2$  ppm which are located in the ppm range for  $\text{Q}^1$  units (Engelhardt and Michel, 1987); it is in good agreement with the two structurally non-equivalent Si sites reported for  $\gamma$ - $\text{Y}_2\text{Si}_2\text{O}_7$  by Batalieva and Pyatenko (1972). However, the  $^{89}\text{Y}$  MAS-NMR spectrum of  $\gamma$ - $\text{Y}_2\text{Si}_2\text{O}_7$  (Becerro *et al.*, 2004) shows a single Y resonance at 118.14 ppm with a fwhm of 60.0 Hz, indicating the presence of a unique Y site in the structure, and in obvious disagreement with the crystallographic description of Batalieva and Pyatenko (1972). A further crystal refinement is necessary in order to clarify the structure of this polymorph.

### $\alpha$ - $\text{Y}_2\text{Si}_2\text{O}_7$ Polymorph

The first unindexed diffraction data for this compound is given in JCPDS chart 21-1457. This chart has been deleted by JCPDS chart 38-223, which shows the indexing on the basis of a triclinic unit cell with space group  $\text{P-1}$  and dimensions:  $a = 6.59$  Å,  $b = 6.60$  Å,  $c = 12.25$  Å,  $\alpha = 94.0^\circ$ ,  $\beta = 89.2^\circ$  and  $\gamma = 93.1^\circ$ . No structural study (in terms of atomic positions) has been reported for  $\alpha$ - $\text{Y}_2\text{Si}_2\text{O}_7$ ; the structural arrangement of the  $\alpha$ -type polymorph has only been established, to our knowledge, for two rare earth disilicates, namely  $\alpha$ - $\text{Ho}_2\text{Si}_2\text{O}_7$  (Felsche, 1972) (ICSD 23619) and  $\alpha$ - $\text{Dy}_2\text{Si}_2\text{O}_7$  (Fleet and Liu, 1983) (ICSD 280408). The  $\alpha$ - $\text{Ho}_2\text{Si}_2\text{O}_7$  structural data are expected to be very close to those of  $\alpha$ - $\text{Y}_2\text{Si}_2\text{O}_7$  given the similar ionic radius of Y(III) and Ho(III) (0.900 Å and 0.901 Å, respectively, in 8-fold coordination) (Shannon, 1976). We have represented, in Fig. 2(a), the unit cell corresponding to the  $\alpha$ -polymorph

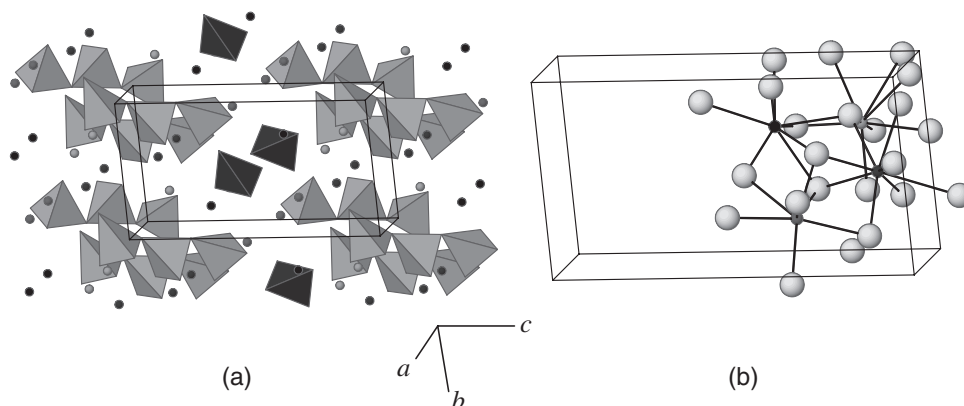


FIGURE 2 (a) The crystal structure of  $\alpha$ - $\text{Y}_2\text{Si}_2\text{O}_7$  based on the data of Felsche (1972). Dark isolated tetrahedra represent  $(\text{SiO}_4)^{4-}$  while the  $(\text{Si}_3\text{O}_{10})$  groups are represented by three light linked tetrahedra. The spheres represent the four crystallographically different Y sites. (b) Detail of the coordination of Y to O.

based on the data of  $\alpha$ - $\text{Ho}_2\text{Si}_2\text{O}_7$ . The striking feature in this structure is the isolated chain-like  $(\text{Si}_3\text{O}_{10})$  groups plus additional  $\text{SiO}_4$  tetrahedra, whereas all the other rare-earth disilicate structure types contain  $\text{Si}_2\text{O}_7$  double tetrahedral groups. The  $\alpha$ -polymorph therefore possesses the average pyrosilicate composition but a different degree of tetrahedra condensation. There are four Si sites and four Y sites in the unit cell, the latter are illustrated in Fig. 2b. The coordination spheres of both cations have been confirmed by spectroscopic methods: the  $^{29}\text{Si}$  MAS-NMR spectrum of  $\alpha$ - $\text{Y}_2\text{Si}_2\text{O}_7$  shows four Si resonances (Parmentier *et al.*, 2000), and the  $^{89}\text{Y}$  MAS-NMR spectrum exhibits, as well, four peaks (Becerro *et al.*, 2004).

### $\beta$ - $\text{Y}_2\text{Si}_2\text{O}_7$ Polymorph

$\beta$ - $\text{Y}_2\text{Si}_2\text{O}_7$  is isostructural with the natural-occurring mineral thorveitite ( $\text{Sc}_2\text{Si}_2\text{O}_7$ ). It crystallises in the monoclinic system, with space group  $C2/m$ . JCPDS charts of  $\beta$ - $\text{Y}_2\text{Si}_2\text{O}_7$  are 21-1454, deleted by 22-1103, deleted in turn by 38-0440. The latter gives the following unit cell dimensions:  $a = 6.875 \text{ \AA}$ ,  $b = 8.970 \text{ \AA}$ ,  $c = 4.721 \text{ \AA}$ ,  $\beta = 101.74^\circ$ . Structural data for  $\beta$ - $\text{Y}_2\text{Si}_2\text{O}_7$  have been recently published (Redhammer and Roth, 2003). Figure 3a shows the unit cell based on their data. It consists of a single Si site and a single RE site; the diortho groups  $\text{Si}_2\text{O}_7$  show Si–O–Si bond angles of  $180^\circ$  (due to the symmetry of the unit cell) and the RE atoms are in octahedral coordination (Fig. 3b). In this case, the bridging oxygen is not involved in the Y octahedron. The single nature of the crystallographic Si and Y sites in the  $\beta$ - $\text{Y}_2\text{Si}_2\text{O}_7$  unit cell has been confirmed by the unique resonance reported by Parmentier *et al.* (2000) in the  $^{29}\text{Si}$  MAS-NMR spectrum of  $\beta$ - $\text{Y}_2\text{Si}_2\text{O}_7$  and by the single peak in the  $^{89}\text{Y}$  MAS-NMR spectrum of this polymorph (Dupree *et al.*, 1988; Becerro *et al.*, 2004).

### $\gamma$ - $\text{Y}_2\text{Si}_2\text{O}_7$ Polymorph

The following JCPDS charts show diffraction data indexed in space group  $P2_1/a$  (no. 14) for  $\gamma$ - $\text{Y}_2\text{Si}_2\text{O}_7$ : 20-1416 deleted by 40-34, deleted by 42-167. The latter gives

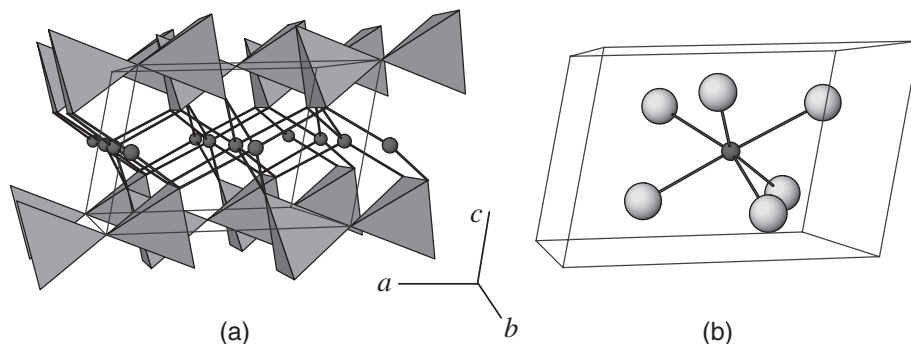


FIGURE 3 (a) The crystal structure of  $\beta\text{-Y}_2\text{Si}_2\text{O}_7$  based on the data of Redhammer and Roth (2003). Polyhedra represent diortho groups  $(\text{Si}_2\text{O}_7)^{6-}$  and the spheres represent the single Y site. (b) Detail of the coordination of Y to O.

the following unit cell dimensions:  $a = 5.579 \text{ \AA}$ ,  $b = 10.857 \text{ \AA}$ ,  $c = 4.696 \text{ \AA}$ ,  $\beta = 95.99^\circ$ . On the other hand, two different structural studies of  $\text{Y}_2\text{Si}_2\text{O}_7$  with space group no. 14 exist in the literature. The first one (ICSD chart 28212) (Batalieva and Pyatenko, 1968) contains structural data of  $\text{Y}_2\text{Si}_2\text{O}_7$  with space group  $P2_1/a$ , but the theoretical X-ray diffraction pattern, calculated with the help of the GSAS software (Larson and Von Dreele, 1994), does not coincide with the data in any of the JCPDS charts mentioned above. In addition, the structure is not the same as that reported for the  $\gamma$  polymorph of other rare earth disilicates like  $\gamma\text{-Ho}_2\text{Si}_2\text{O}_7$  and  $\gamma\text{-Er}_2\text{Si}_2\text{O}_7$  (Felsche, 1973). The second study, owed to Christensen *et al.* (1997) (no ICSD chart found), reports the structure of  $\gamma\text{-Y}_2\text{Si}_2\text{O}_7$  with monoclinic symmetry and space group  $P2_1/c$  (another setting of space group no. 14). In this case, the theoretical X-ray diffraction pattern is in agreement with the JCPDS chart 42-167. Figure 4(a) shows the unit cell of  $\gamma\text{-Y}_2\text{Si}_2\text{O}_7$  based on the data from Christensen *et al.* (1997); it contains a unique Si site and a unique Y site. Si atoms occupy tetrahedral holes, forming  $\text{Si}_2\text{O}_7$  groups while the Y site shows octahedral coordination (Fig. 4b). Bridging oxygens of the disilicate unit do not participate in the Y octahedron and the Si–O–Si bond angle is around  $172^\circ$ . The  $^{29}\text{Si}$  MAS-NMR spectrum of  $\gamma\text{-Y}_2\text{Si}_2\text{O}_7$  (Parmentier *et al.*, 2000) shows a single peak corresponding to the unique silicon site in the crystal structure. Likewise, the  $^{89}\text{Y}$  MAS-NMR spectrum (Dupree *et al.*, 1988; Becerro *et al.*, 2004) shows a narrow and single  $^{89}\text{Y}$  resonance which confirms the single nature of the Y site in unit cell.

### $\delta\text{-Y}_2\text{Si}_2\text{O}_7$ Polymorph

Unindexed data for  $\delta\text{-Y}_2\text{Si}_2\text{O}_7$  were included in JCPDS 21-1460 and 22-994; the latter refers to “alpha- $\text{Y}_2\text{Si}_2\text{O}_7$ ” but the position and intensity of the reflections correspond to the  $\delta$ -polymorph; this has been deleted by JCPDS 45-43, with indexing in the orthorhombic space group  $\text{Pna}2_1$  (no. 33) and cell dimensions:  $a = 13.6 \text{ \AA}$ ,  $b = 5.01 \text{ \AA}$  and  $c = 8.15 \text{ \AA}$ . The chart does not specify the polymorph type but its primary reference indicates  $\delta\text{-Y}_2\text{Si}_2\text{O}_7$ . Finally, JCPDS charts 42-168 and 82-0732 contain experimental and calculated data, respectively, for  $\delta\text{-Y}_2\text{Si}_2\text{O}_7$ , with cell dimensions very similar to those described above. Regarding crystal structure analyses, two different studies

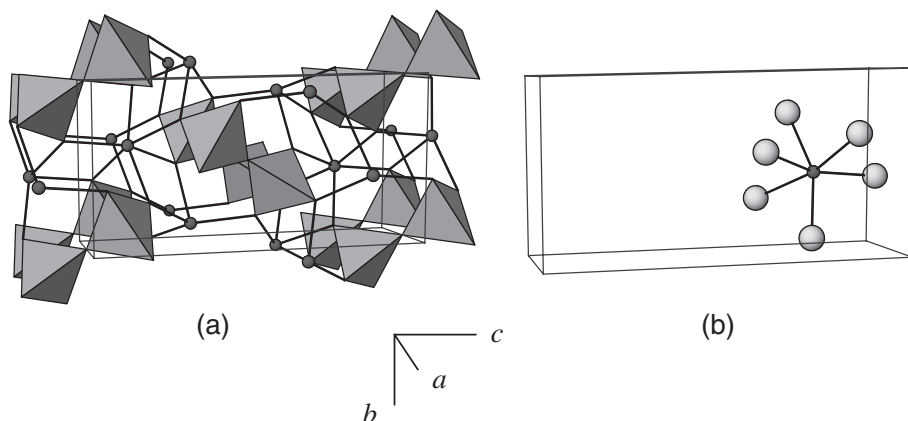


FIGURE 4 (a) The crystal structure of  $\gamma$ - $\text{Y}_2\text{Si}_2\text{O}_7$  based on the data of Christensen *et al.* (1997). Polyhedra represent diortho groups ( $\text{Si}_2\text{O}_7$ )<sup>6-</sup> and the spheres represent the single Y site. and (b) Detail of the coordination of Y to O.

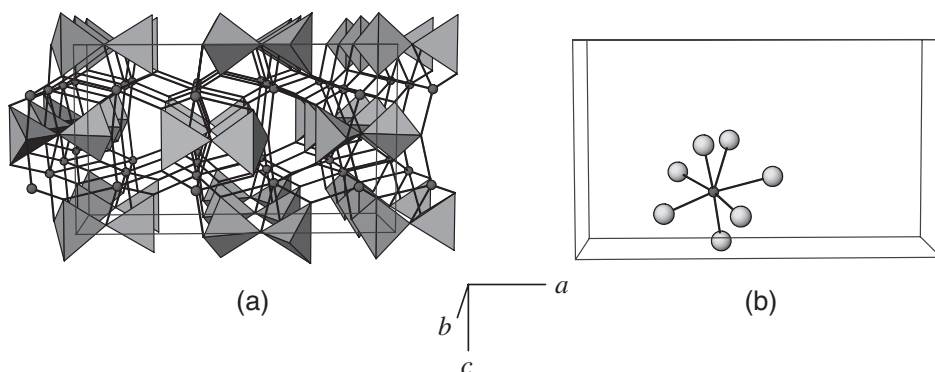


FIGURE 5 (a) The crystal structure of  $\delta$ - $\text{Y}_2\text{Si}_2\text{O}_7$  based on on the data of Dias *et al.* (1990). Polyhedra represent diortho groups ( $\text{Si}_2\text{O}_7$ )<sup>6-</sup> and the spheres represent the single Y site. (b) Detail of the coordination of Y to O.

have been published. The first one, by Dias *et al.* (1990) (ICSD chart 33721), describes the unit cell in terms of the orthorhombic space group Pnam (no. 62) and assigns a unique site to Y, with CN 7. The second one, by Christensen (1994) (ICSD chart 74778), uses the orthorhombic space group Pna2<sub>1</sub> and assigns two different crystallographic sites to Y, both with CN 7. We have recently clarified the structure by using <sup>89</sup>Y MAS-NMR spectroscopy, which informs directly on the local environment of the Y atoms. The spectrum of  $\delta$ - $\text{Y}_2\text{Si}_2\text{O}_7$  exhibits a single Y resonance at 121.14 ppm with a narrow linewidth (Becerro *et al.*, 2004). This result confirms the single nature of the Y site in the crystal structure and reinforces the description of Dias *et al.* (1990). Figure 5(a) shows the  $\delta$ - $\text{Y}_2\text{Si}_2\text{O}_7$  unit cell based on the data from Dias *et al.* (1990); the structure consists of  $\text{Si}_2\text{O}_7$  groups with a Si–O–Si bond angle of 158°. In this case, the bridging oxygen forms part of the Y coordination polyhedron, which shows CN 7 (Fig. 5b). On the other hand, the presence of two different crystallographic



Si sites in the structure, as revealed by both diffraction studies, is confirmed by the  $^{29}\text{Si}$  MAS-NMR spectrum of this polymorph with two well separated  $^{29}\text{Si}$  resonances (Parmentier *et al.*, 2000).

### **$\text{Y}_2\text{SiO}_5$ Polymorphs**

$\text{Y}_2\text{SiO}_5$  polymorphs contain isolated tetrahedra and belong to the orthosilicates group called oxyorthosilicates because, in addition to the  $(\text{SiO}_4)^{4-}$  anion, they contain non-silicon-bonded oxygen ions in the structure. All binary compounds of composition  $1\text{RE}_2\text{O}_3 \cdot 1\text{SiO}_2$  (RE = rare earth) belong to this group, which displays two different structure types. One is stable for the large RE La to Tb (called X1 structures) and the other comprises the smaller RE Dy to Lu.  $\text{Y}_2\text{SiO}_5$  displays both structure types: X1, stable at temperatures below  $\sim 1190^\circ\text{C}$  and X2, stable at higher temperatures.

#### **$\text{X1-Y}_2\text{SiO}_5$ Polymorph**

The first diffraction chart reported for this polymorph (JCPDS 21-1456) contains unindexed data and has been deleted by JCPDS chart 41-0004, which contains indexing in the monoclinic space group  $P2_1/c$  with unit cell parameters  $a = 9.012(8)\text{ \AA}$ ,  $b = 6.979(6)\text{ \AA}$ ,  $c = 6.630(6)\text{ \AA}$  and  $\beta = 106.7^\circ$ . The X1- $\text{Y}_2\text{SiO}_5$  crystal structure has been recently published (Wang *et al.*, 2001) based on a very similar unit cell, with a unique Si site and two different Y sites, the latter equally populated (Fig. 6a). Y shows high coordination numbers: 7 and 9 (Fig. 6b). We have recently reported the  $^{89}\text{Y}$  MAS-NMR spectrum of X1- $\text{Y}_2\text{SiO}_5$  (Becerro *et al.*, 2004), which shows two well resolved Y resonances at 215.2 and 75.2 ppm, in agreement with the crystallographic description of this polymorph. In order to confirm the single nature of the Si site in the structure, and given the lack of a short-range order study of this polymorph in the literature, we have registered the  $^{29}\text{Si}$  MAS-NMR spectrum of this polymorph, which has been included in Fig. 6(c). It shows a single  $^{29}\text{Si}$  resonance with a chemical shift of  $-82.3\text{ ppm}$ , which falls in the range for  $\text{Q}^0$  units and does agree well with the diffraction data of this polymorph.

#### **$\text{X2-Y}_2\text{SiO}_5$ Polymorph**

The first single crystal investigation was carried out by Michel *et al.* (1967) (ICSD chart 27003), who described the crystal on the basis of a monoclinic cell (space group  $B2/b$ ,  $a = 14.59\text{ \AA}$ ,  $b = 10.52\text{ \AA}$ ,  $c = 6.82\text{ \AA}$ ,  $\gamma = 122.25^\circ$ ). The structure was subsequently refined by Maksimov *et al.* (1968) (ICSD chart 283205) and Maksimov *et al.* (1970) (ICSD chart 28021), in terms of the equivalent cells  $I2/c$  and  $I2/a$ , respectively, with slightly smaller dimensions than the former ( $a = 10.41\text{ \AA}$ ,  $b = 6.72\text{ \AA}$ ,  $c = 12.49\text{ \AA}$ ,  $\beta = 102.65^\circ$ ). Experimental diffraction patterns are included in JCPDS charts 21-1458 (not indexed), 21-1461 (not indexed), 22-992 and 36-1476 both indexed in space group  $I2/a$ , with similar cell dimensions to those of Maksimov *et al.* (1968, 1970). Finally, patterns calculated based on the analysis of Michel *et al.* (1967), Maksimov *et al.* (1968) and Maksimov (1970) are included in JCPDS charts 74-1266, 74-2158 and 74-2011, respectively. Figure 7(a) displays the X2- $\text{Y}_2\text{SiO}_5$  crystal structure with data from ICSD 28021. The unit cell contains a unique Si site and two crystallographically different Y sites with coordination numbers 6 and 7 and equal populations.

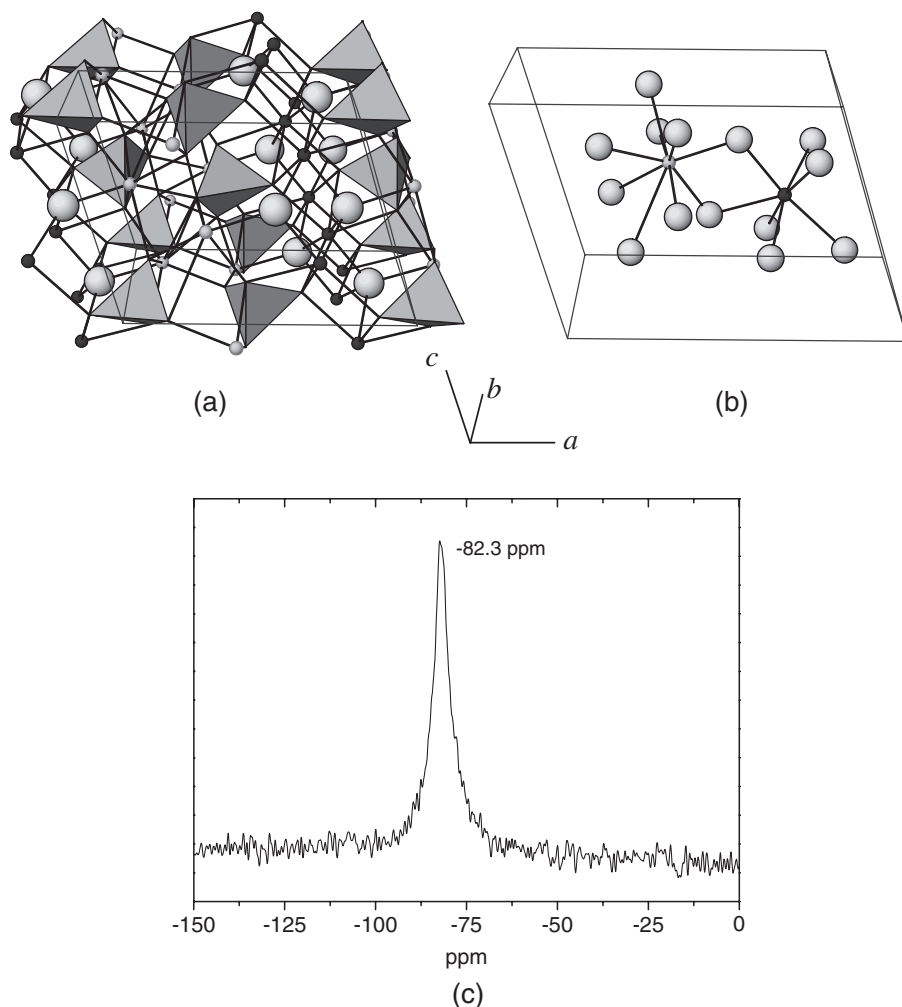


FIGURE 6 (a) The crystal structure of  $X1-Y_2SiO_5$  based on the data of Wang *et al.* (2001). Tetrahedra represent  $(SiO_4)^{4-}$  units, the small dark and light grey spheres represent the two crystallographically different Y sites and the big spheres are not silicon-bonded oxygen ions. (b) Detail of the coordination of Y to O. (c)  $^{29}Si$  MAS-NMR spectrum of  $X1-Y_2SiO_5$ .

The local environment of both cations is confirmed by the corresponding MAS-NMR spectra of the compound: the  $^{89}Y$  MAS-NMR spectrum shows a double  $^{89}Y$  resonance (Becerro *et al.*, 2004) while the  $^{29}Si$  MAS-NMR spectrum exhibit a single peak corresponding to the unique Si site in the unit cell of this polymorph (Dupree *et al.*, 1988).

## EXPERIMENTAL

*Synthesis of the  $X1-Y_2SiO_5$  compound* The sample was synthesised following the ceramic method.  $SiO_2$  (Silica fumed 99.8%, Sigma) and  $Y(NO_3)_3 \cdot 6H_2O$  (Aldrich) in molar ratio  $1SiO_2:2Y(NO_3)_3 \cdot 6H_2O$  were mixed in excess ethanol with magnetic



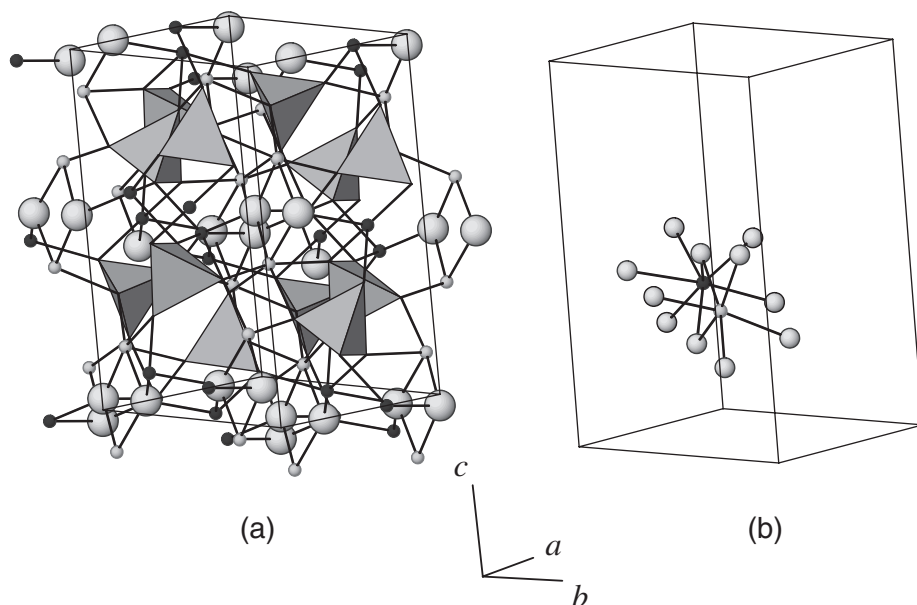


FIGURE 7 (a) The crystal structure of  $X_2Y_2Si_2O_7$  based on the data of Maksimov *et al.* (1970). Tetrahedra represent  $(SiO_4)^{4-}$  units, the small dark and light grey spheres represent the two crystallographically different Y sites and the big spheres are not silicon-bonded oxygen ions. (b) Detail of the coordination of Y to O.

stirring for 2 h. The solution was dried in the oven at  $60^\circ\text{C}$  for 24 h and the nitrate were then removed by heating up to  $500^\circ\text{C}$  for 1 h at  $1^\circ\text{C}/\text{min}$ . The powder was annealed at  $1050^\circ\text{C}$  for 5 days in air, at a heating rate of  $5^\circ\text{C}/\text{min}$ .

**$^{29}\text{Si}$  MAS-NMR spectrum** The  $^{29}\text{Si}$  Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) spectrum of the reaction product was collected in a Bruker DRX400 (9.39 T) spectrometer using 4 mm zirconia rotors spinning at 12 KHz.  $30^\circ$  pulses and 3 s delay time were used.

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